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D-allose, D-altrose, D-glucose, D-mannose, D-glucose, D-idose, D-galactose, D-talose, L-fucose or L-rhamnose; examples of a ketopentose are D-ribulose or D-xylulose; examples of a tetrose are D-erythrose or threose; and examples of a ketohexose are D-psicose, D-fructose, 5 D-sorbitose or D-tagatose. Examples of a disaccharide are trehalose, maltose, somaltose, cellobiose, gentiobiose, saccharose, lactose, chitobiose, N,N-diacylchitobiose, palatinose or sucrose. Raffinose, panose or maltotriose may be mentioned as an example of a trisaccharide. Examples of 10 an oligosaccharide are maltotetraose, maltohexaose, chitoheptaose and furthermore cyclic oligosaccharides, such as cyclodextrins.

Cyclodextrins contain 6 to 8 identical units of α -1,4-glucose. Some examples are α -, β - and γ -cyclodextrin, derivatives of such cyclodextrins, for example hydroxypropylcyclodextrins, and branched cyclodextrins.

The macromers according to this embodiment of invention can be prepared by processes known per se, for example as follows.

In a first step, a polysiloxane containing at least one primary amino- or hydroxyalkyl group is reacted with a carbohydrate lactone, an amide or ester bond being formed and a compound of the formula (XIIa) or (XIIb) being formed:



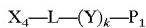
(XIIa)



(XIIb)

in which the variables are as defined above and Z is a group X₁,

after which the compound (XII) is reacted with an unsaturated polymerizable compound of the formula (XIII):

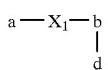


(XIII)

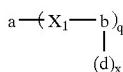
in which X₄ is a group which is coreactive with a hydroxyl or amino group of segment (b), an X₃ group of a segment (d) according to formula (II) being formed from such a reaction, where X₄ is preferably —COOH, —COOR₁₀, —COCl or —NCO, in which R₁₀ is alkyl, or is aryl which is unsubstituted or substituted by lower alkyl or lower alkoxy, and the other variables are as defined above,

after which a macromer according to the formula (IV) or (V) is formed

(IV)



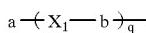
(V)



in which the segments (d) are incorporated terminally or pendently.

Another process starts from a polysiloxane (a) which contains terminal primary amino- or hydroxyalkyl groups and is reacted with a carbohydrate dilactone to form linear structures of the formula (XIV):

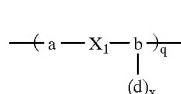
(XIV)



in which the variables are as defined and preferred above, after which a compound of the formula (XIV) is reacted with

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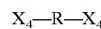
a compound of the formula (XIII) analogously to the above process to give a macromer of the formula (VI):



(VI)

in which the variables are as defined and preferred above.

Another process starts from a polysiloxane (a) which contains terminal primary amino- or hydroxyalkyl groups and is initially reacted with a bifunctional compound of the formula (XV):

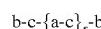


(XV)

in which X₄ is a group which is coreactive with a hydroxyl or amino group of segment (a), an X₂ group of a segment (c) being formed from such a reaction, where X₄ is preferably

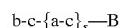
—COOH, —COOR₁₀, —COCl or —NCO, in which R₁₀ is alkyl, or aryl which is unsubstituted or substituted by lower alkyl or lower alkoxy, and R is as defined above,

after which this intermediate is reacted with a polyol which carries no lactone group to give a compound of the formula (XVI):



(XVI)

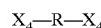
in which the variables are as defined and preferred above, after which the compound of the formula (XVI) is reacted with a compound of the formula (XIII) to give a macromer of the formula (X):



(X)

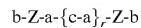
in which s is an integer from 1 to 10, preferably from 1 to 7, and in particular from 1 to 3; B is a segment (a) or (b); and the above preferences apply to the number of segments (d) which are bonded to a segment (b).

Another process starts from a bifunctional compound of the formula (XV):



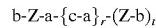
(XV)

which is reacted with an excess of polysiloxane (a) to give an $-a-(c-a)_r-$ sequence, in which the above meanings apply, after which, in a second step, the intermediate is reacted with a polyol which carries no lactone to give a compound of the formula (XVII):



(XVII)

after which the compound (XVII) is reacted with the compound (XIII) to give a macromer of the formula (VIII):



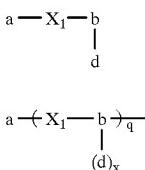
(VIII)

in which r is an integer from 1 to 10, preferably from 1 to 7, and in particular from 1 to 3; t is 0 or 1, and is preferably 1; in which a linear (c-a) chain, which may or may not be terminated by a segment (b), is present (t=1); and the above preferences apply to the total number of segments (d), which are preferably bonded to a segment (b).

Another process starts from a carbohydrate lactone which is reacted in a first step with a compound of the formula (XIII), the lactone function being retained, after which the intermediate is reacted with a polysiloxane containing at least one amino or hydroxyl group to give a compound of the formula (IV) or (V):

5,965,631

37



(IV)

(V)

in which q is typically 1 or 2, and in which the above meanings and preferences otherwise apply, and the segments (d) are incorporated terminally or pendently.

The present embodiment of the invention furthermore relates to the intermediates which are novel and which occur during synthesis of the macromers according to the invention.

The invention therefore furthermore relates to a compound of the formula (XIIa):



(XIIa)

in which q is greater than 1,

(a) is derived from a polysiloxane as defined by formula (I) above and

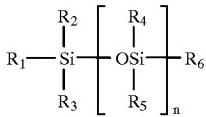
(b) is derived from a carbohydrate dilactone.

An embodiment of the invention furthermore relates to a compound of the formula (XIIb):



(XIIb)

in which Z, (b) and q are as defined and preferred above, but with the proviso that a segment (a) is derived from a compound of the formula (III):



(III)

in which n is an integer from 5 to 500;

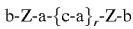
99.8–25% of the radicals R₁, R₂, R₃, R₄, R₅ and R₆ independently of one another are alkyl and 0.2–75% of the radicals R₁, R₂, R₃, R₄, R₅ and R₆ independently of one another are partly fluorinated alkyl, aminoalkyl, alkenyl, aryl, cyanoalkyl, alk-NH—Alk—NH₂ or alk-(OCH₂CH₂)_m—(OCH₂)_p—OR₇ in which R₇ is hydrogen or lower alkyl, alk is alkylene and m and p independently of one another are an integer from 0 to 10, one molecule containing at least one primary amino or hydroxyl group and at least one partly fluorinated alkyl group. The invention furthermore relates to a compound of the formula (XVI):



(XVI)

in which a segment (b) is derived from a polyol which carries no lactone and the other variables are as defined and preferred above.

An embodiment of the invention furthermore relates to a compound of the formula (XVII):



(XVII)

in which a segment (b) is derived from a polyol which carries no lactone and the other variables are as defined and preferred above.

38

A siloxane (a) containing at least one primary amino or hydroxyl group is, for example, commercially obtainable. Examples are KF-6002, KF-8003, X-22-161C (Shin Etsu) or GP4 (Genesee). Other siloxanes can be synthesized with the aid of published processes.

A polyol (b) required for the synthesis is as a rule commercially obtainable. Examples are gluconolactone or lactobionolactone. Otherwise, they can be synthesized with the aid of a published process.

10 The compounds according to the invention can be prepared in the presence or absence of a solvent. A solvent which is largely inert, i.e., does not participate in the reaction, is advantageously used. Suitable examples of these are ethers, such as tetrahydrofuran (THF), 1,2-

15 dimethoxyethane, diethylene glycol dimethyl ether or dioxane, halogenated hydrocarbons, such as chloroform or methylene chloride, bipolar aprotic solvents, such as acetonitrile, acetone, dimethylformamide (DMF) or dimethyl sulfoxide (DMSO), hydrocarbons, such as toluene or xylene, and furthermore pyridine or N-methylmorpholine.

20 The reactants are advantageously employed in stoichiometric amounts for the preparation of the compounds according to the invention. The reaction temperature can be, for example, from -30° C. to 150° C. The range from 0° C. to 40° C. is a preferred temperature range. The reaction times here are in the range from about 15 minutes to 7 days, preferably in the region of about 12 hours. If necessary, the reaction is carried out under argon or nitrogen as an inert gas. A suitable catalyst is advantageously added for urethane-forming reactions, for example dibutyltin dilaurate (DBTDL).

25 The present invention furthermore relates to a polymer comprising a polymerization product of at least one macromer according to the invention as defined above and, if appropriate, at least one vinylic comonomer (a).

30 The preferred composition of a polymer according to the invention comprises a weight content, with respect to the total polymer, of a macromer according to the invention in the range from 100 to 0.5%, in particular in the range from 80 to 10%, and preferably in the range from 70 to 30%.

35 In a preferred polymer comprising a polymerization product of at least one macromer according to the invention, comonomer (a) is absent and the polymer is preferably a homopolymer.

40 A comonomer (a) which is contained in a polymer according to the invention can be hydrophilic or hydrophobic or a mixture of both. Suitable comonomers include, in particular, those which are usually used for the preparation of contact lenses and biomedical materials. A hydrophobic comonomer (a) is understood as meaning monomers which typically give, as a homopolymer, polymers which are water-insoluble and can absorb less than 10% by weight of water.

45 Analogously, a hydrophilic comonomer (a) is understood as meaning a monomer which typically gives, as a homopolymer, a polymer which is water-soluble or can absorb at least 10% by weight of water.

50 Suitable hydrophobic comonomers (a) include, without this list being exhaustive, C₃–C₁₈alkyl and C₃–C₁₈cycloalkyl acrylates and methacrylates, C₃–Cl₈alkylacrylamides and methacrylamides, acrylonitrile, methacrylonitrile, vinyl C₁–C₁₈alkanoates, C₂–C₁ alkenes, C₂–C₁₈haloalkenes, styrene, lower alkyl styrene, lower alkyl vinyl ethers, C₂–C₁₀perfluoroalkyl acrylates and methacrylates or correspondingly partly fluorinated acrylates and methacrylates, C₃–C₁₂perfluoroalkyl-ethyl-thiocarbonylaminooethyl acrylates and methacrylates, acryloxy- and methacryloxy-alkylsiloxanes,

39

N-vinylcarbazole and C₁-C₁₂alkyl esters of maleic acid, fumaric acid, itaconic acid, mesaconic acid and the like. Preferred comonomers are, for example, acrylonitrile, C₁-C₄alkyl esters of vinylically unsaturated carboxylic acids having 3 to 5 carbon atoms, or vinyl esters of carboxylic acids having up to 5 carbon atoms.

Examples of suitable hydrophobic comonomers (a) include methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, isobutyl acrylate (IBA), isoctyl acrylate (OA), isodecyl acrylate (DA), cyclohexyl acrylate, 2-ethylhexyl acrylate (EHA), methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl acrylate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate, styrene, chloroprene, vinyl chloride, vinylidene chloride, acrylonitrile, 1-butene, butadiene, methacrylonitrile, vinyl toluene, vinyl ethyl ether, perfluorohexyethylthiocarbonylaminoethyl methacrylate, isobornyl methacrylate, trifluoroethyl methacrylate, hexafluoroisopropyl methacrylate, hexafluorobutyl (meth)acrylate (HFBMA and HFBA), tris(trimethylsilyloxy)silyl-propyl methacrylate (TRIS), 3-methacryloxypropylpentamethyldisiloxane and bis(methacryloxypropyl) tetramethyldisiloxane. Preferred examples of hydrophobic comonomers (a) are methyl methacrylate, IBA, HFBA, HFBMA, OA, EHA, DA, TRIS and acrylonitrile.

Suitable hydrophilic comonomers (a) include, without this list being conclusive, hydroxyl-substituted lower alkyl acrylates and methacrylates, acrylamide, methacrylamide, lower alkylacrylamides and -methacrylamides, ethoxylated acrylates and methacrylates, hydroxyl-substituted lower alkylacrylamides and -methacrylamides, hydroxyl-substituted lower alkyl vinyl ethers, sodium vinylsulfonate, sodium styrenesulfonate, 2-acrylamido-2-methylpropanesulfonic acid, N-vinylpyrrole, N-vinyl-2-pyrrolidone, 2-vinylloxazoline, 2-vinyl-4,4'-dialkyloxazolin-5-one, 2- and 4-vinylpyridine, vinylically unsaturated carboxylic acids having a total of 3 to 5 carbon atoms, amino-lower alkyl (where the term "amino" also includes quaternary ammonium), mono-lower alkylamino-lower alkyl and di-lower alkylamino-lower alkyl acrylates and methacrylates, allyl alcohol and the like. Preferred comonomers are, for example, N-vinyl-2-pyrrolidone, acrylamide, methacrylamide, hydroxyl-substituted lower alkyl acrylates and methacrylates, hydroxyl-substituted lower alkylacrylamides and -methacrylamides and vinylically unsaturated carboxylic acids having a total of 3 to 5 carbon atoms.

Examples of suitable hydrophilic comonomers (a) include hydroxyethyl methacrylate (HEMA), hydroxyethyl acrylate, hydroxypropyl acrylate, trimethylammonium-2-hydroxypropyl methacrylate hydrochloride (Blemer® QA, for example from Nippon Oil), dimethylaminoethyl methacrylate (DMAEMA), dimethylaminoethyl methacrylamide, acrylamide, methacrylamide, N,N-dimethylacrylamide (DMA), allyl alcohol, vinylpyridine, glycerol methacrylate, N-(1,1-dimethyl-3-oxobutyl)acrylamide, N-vinyl-2-pyrrolidone (NVP), acrylic acid, methacrylic acid and the like.

Preferred hydrophilic comonomers (a) are 2-hydroxyethyl methacrylate, dimethylaminoethyl methacrylate, trimethylammonium-2-hydroxypropyl methacrylate hydrochloride, N,N-dimethylacrylamide and N-vinyl-2-pyrrolidone.

The polymers according to the invention are built up in a manner known per se from the corresponding monomers (the term monomers here also including a macromer according to the invention) by a polymerization reaction with which the expert is familiar. Usually, a mixture of the

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abovementioned monomers is heated, with the addition of an agent which forms free radicals. Such an agent which forms free radicals is, for example, azoisobutyronitrile (AIBN), potassium peroxodisulfate, dibenzoyl peroxide, hydrogen peroxide or sodium percarbonate. If the compounds mentioned are heated, for example, free radicals are then formed, by homolysis, and can then, for example, initiate a polymerization.

A polymerization reaction can particularly preferably be carried out using a photoinitiator. Photopolymerization is the term used in this case. For photopolymerization, a photoinitiator which can initiate free radical polymerization and/or crosslinking by the use of light is suitably added. Examples of this are familiar to the expert, and specifically, suitable photoinitiators are benzoin methyl ether, 1-hydroxycyclohexyl phenyl ketone and Darocur and Irgacur types, preferably Darocur 1173® and Darocur 2959®. Reactive photoinitiators which can be incorporated, for example, into a macromer or can be used as a special comonomer (a) are also suitable. Examples of these are to be found in EP 632 329. The photopolymerization can then be triggered off by actinic radiation, for example light, in particular UV light of a suitable wavelength. The spectral requirements can be controlled accordingly, if appropriate, by addition of suitable photosensitizers.

Polymerization can be carried out in the presence or absence of a solvent. Suitable solvents are in principle all solvents which dissolve the monomers used, for example water, alcohols, such as lower alkanols, for example ethanol or methanol, and furthermore carboxylic acid amides, such as dimethylformamide, dipolar aprotic solvents, such as dimethyl sulfoxide or methyl ethyl ketone, ketones, for example acetone or cyclohexanone, hydrocarbons, for example toluene, ethers, for example THF, dimethoxyethane or dioxane, and halogenated hydrocarbons, for example trichloroethane, and also mixtures of suitable solvents, for example mixtures of water with an alcohol, for example a water/ethanol or a water/methanol mixture.

If appropriate, a polymer network can be intensified by addition of a so-called crosslinking agent, for example a polyunsaturated comonomer (b). The invention furthermore relates to a polymer comprising the polymerization product of a macromer according to the invention with, if appropriate, at least one vinylic comonomer (a) and with at least one comonomer (b).

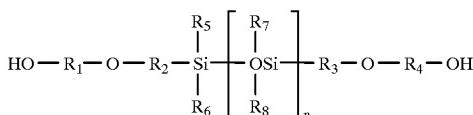
Examples of typical comonomers (b) are, for example, allyl(meth)acrylate, lower alkylene glycol di(meth)acrylate, poly lower alkylene glycol di(meth)acrylate, lower alkylene di(meth)acrylate, divinyl ether, divinyl sulfone, di- or trivinylbenzene, trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, bisphenol A di(meth)acrylate, methylenebis(meth)acrylamide, triallyl phthalate or diallyl phthalate.

The amount of comonomer (b) used is expressed in the weight content with respect to the total polymer and is in the range from 20 to 0.05%, in particular in the range from 10 to 0.1%, and preferably in the range from 2 to 0.1%.

4. "Material D"

Another advantageous embodiment of the present invention relates to the use of a siloxane-containing macromer which is formed from a poly(dialkylsiloxane) dialkoxyalkanol having the following structure:

5,965,631

41

where n is an integer from about 5 to about 500, preferably about 20 to 200, more preferably about 20 to 100;

the radicals R₁, R₂, R₃, and R₄, independently of one another, are lower alkylene, preferably C₁-C₆ alkylene, more preferably C₁-C₃ alkylene, wherein in a preferred embodiment, the total number of carbon atoms in R₁ and R₂ or in R₃ and R₄ is greater than 4; and

R₅, R₆, R₇, and R₈ are, independently of one another, are lower alkyl, preferably C₁-C₆ alkyl, more preferably C₁-C₃ alkyl.

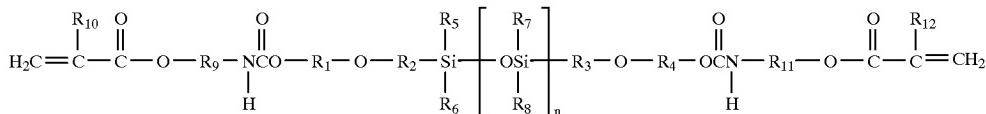
The general structure of the Material D macromer follows:

ACRYLATE-LINK-ALK-O-ALK-PDAS—
ALK-O-ALK-LINK-ACRYLATE

where the ACRYLATE is selected from acrylates and methacrylates; LINK is selected from urethanes and dirurethane linkages, ALK-O-ALK is as defined above (R₁-O-R₂ or R₃O-R₄), and PDAS is a poly(dialkylsiloxane).

For example, a Material D macromer may be prepared by reacting isophorone diisocyanate, 2-hydroxyethyl (meth) acrylate and a poly(dialkylsiloxane) dialkoxyalkanol in the presence of a catalyst.

A preferred Material D macromer may be prepared by reacting a slight excess of isocyanatoalkyl methacrylate, especially isocyanatoethyl methacrylate (IEM), with a poly (dialkylsiloxane) dialkoxyalkanol, preferably poly (dimethylsiloxane) dipropoxyethanol, in the presence of a catalyst, especially an organotin catalyst such as dibutyltin dilaurate (DBTL). The primary resulting structure is as follows:



where

R₉ and R₁₁ are alkylene; preferably C₁-₆ alkylene, more preferably ethylene;

R₁₀ and R₁₂ are methyl or hydrogen.

The "Material D" prepolymer mixture may be formed by mixing the aforementioned siloxane-containing macromer with one or more hydrophilic monomers and a thermoinitiator or a photoinitiator such as Darocur® 1173. A solvent, such as hexanol, is preferably added to homogenize the mixture. Preferably, an appropriate amount of TRIS is added to lower the modulus of elasticity to a desired level. The ionoperm monomer or monomers may be selected from any of the aforementioned ionoperm or hydrophilic monomers. Preferably, the ionoperm monomer is selected from the group consisting of acrylates, methacrylates, acrylamides, methacrylamides and mixtures thereof. More preferably, the ionoperm monomers are selected from dimethylacrylamide (DMA) and methacrylic acid (MAA).

A preferred "Material D" prepolymer mixture, in weight percentages based on total mixture weight, includes about 35 to 60% Material D macromer; about 6 to 25% TRIS; about

42

15 to 35% ionoperm monomer; about 0.1 to 1% photoinitiator; and about 10 to 20% solvent. A more preferred "Material D" prepolymer mixture, in weight percentages based on total mixture weight, includes the following: about 40 to 55% Material D macromer; about 8 to 16% TRIS; about 20 to 30% dimethylacrylamide; about 0.2 to 2% methacrylic acid; about 0.1 to 1% photoinitiator; and about 10 to 20% solvent. A particularly preferred "Material D" prepolymer mixture, in weight percentages based on total mixture weight, includes the following: about 44 to 50% Material D macromer; about 10 to 12% TRIS; about 22 to 26% dimethylacrylamide; about 0 to 1% methacrylic acid; about 0.2 to 0.6% photoinitiator; and about 10 to 20% solvent.

The prepolymer mixture may be formed into lenses and other ophthalmic devices by any of a number of techniques known in the art and disclosed herein. Preferably, the prepolymer mixture is conveyed into a concave half of a lens mold, the convex mold half is mated with the concave mold half, and an appropriate amount of radiation is applied to initiate polymerization. While ultraviolet (UV) radiation is preferred, a number of other energy sources known in the art and disclosed herein may also be used.

The Material D ophthalmic lens is preferably a polymerization product of the following macromeric and monomeric components, based on total weight of polymerizable material:

- (a) about 45 to about 65 percent Material D macromer;
- (b) about 5 to about 25 percent TRIS; and
- (c) about 20 to about 40 percent ionoperm monomer.

The Material D ophthalmic lens is more preferably a polymerization product of the following macromeric and monomeric components, based on total weight of polymerizable material:

- (a) about 50 to about 60 percent Material D macromer;
- (b) about 10 to about 20 percent TRIS; and
- (c) about 25 to about 35 percent ionoperm monomer.

In a preferred embodiment, the Material D ophthalmic lens is a polymerization product of the following macro-

meric and monomeric components, based on total weight of polymerizable material:

- (a) about 50 to about 60 percent Material D macromer;
- (b) about 10 to about 20 percent TRIS;
- (c) about 25 to about 35 percent DMA; and
- (d) up to about 2 percent MAA.

In another preferred embodiment, about 0.2 to 1.0 weight percent MAA is used, together with the components (a), (b), and (c) in the above-cited amounts.

III. Ophthalmically Compatible Surfaces

The ophthalmic lenses of the present invention have a surface which is biocompatible with ocular tissue and ocular fluids during the desired extended period of contact. In one preferred embodiment, the ophthalmic lenses of the present invention include a core material, as defined above, surrounded, at least in part, by a surface which is more hydrophilic and lipophobic than the core material. A hydrophilic surface is desirable in order to enhance the compatibility of the lens with the ocular tissues and tear fluids. As surface hydrophilicity increases, undesirable attraction and adherence of lipids and proteinaceous matter typically

decreases. There are factors other than surface hydrophilicity, such as immunological response, which may contribute to deposit accumulation on the lens. Deposition of lipids and proteinaceous matter causes haze on the lens, thereby reducing visual clarity. Proteinaceous deposits may also cause other problems, such as irritation to the eye. After extended periods of continuous or intermittent wear, the lens must be removed from the eye for cleaning, i.e., deposit removal. Therefore, increased surface hydrophilicity, and concomittent reductions in deposits of biological matter, allows increased wear time.

"Surface treatment processes", as used herein, refers to processes to render a surface more ophthalmically compatible, in which, by means of contact with a vapor or liquid, and/or by means of application of an energy source (1) a coating is applied to the surface of an article, (2) chemical species are adsorbed onto the surface of an article, (3) the chemical nature (e.g., electrostatic charge) of chemical groups on the surface of an article are altered, or (4) the surface properties of an article are otherwise modified.

There are a variety of methods disclosed in the art for rendering a surface of a material hydrophilic. For example, the lens may be coated with a layer of a hydrophilic polymeric material. Alternatively, hydrophilic groups may be grafted onto the surface of the lens, thereby producing a monolayer of hydrophilic material. These coating or grafting processes may be effected by a number of processes, including without limitation thereto, exposing the lens to plasma gas or immersing the lens in a monomeric solution under appropriate conditions.

Another set of methods of altering the surface properties of a lens involves treatment prior to polymerization to form the lens. For example, the mold may be treated with a plasma (i.e., an ionized gas), a static electrical charge, irradiation, or other energy source, thereby causing the prepolymerization mixture immediately adjacent the mold surface to differ in composition from the core of the prepolymerization mixture.

A preferred class of surface treatment processes are plasma processes, in which an ionized gas is applied to the surface of an article. Plasma gases and processing conditions are described more fully in U.S. Pat. Nos. 4,312,575 and 4,632,844, which are incorporated herein by reference. The plasma gas is preferably a mixture of lower alkanes and nitrogen, oxygen or an inert gas.

In a preferred embodiment, the lens is plasma treated in the presence of a mixture of (a) a C₁₋₆ alkane and (b) a gas selected from the group consisting of nitrogen, argon, oxygen, and mixtures thereof. In a more preferred embodiment, the lens is plasma treated in the presence of a mixture of methane and air.

IV. Utility

A. Ophthalmic Lenses

The novel polymers or crosslinked polymers can be converted into ophthalmic moldings in a manner known in the art, in particular into contact lenses, for example by carrying out the photopolymerization or photocrosslinking of the novel polymers in a suitable contact lens mold. Examples of novel ophthalmic moldings, in addition to contact lenses, include without limitation thereto, contact lenses for vision correction, contact lenses for eye color modification, ophthalmic drug delivery devices, ophthalmic wound healing devices, and the like.

B. Contact Lenses

A specific embodiment of the invention is directed to contact lenses which comprise essentially a novel polymer or polymeric network. Such contact lenses have a range of

unusual and extremely advantageous properties. Amongst these properties are, for example, their excellent compatibility with the human cornea (if necessary after suitable surface treatment (coating)) and with tear fluid, which is based on a balanced ratio between water content and water permeability, oxygen permeability and mechanical and adsorptive properties. This balance of desirable properties results in high comfort and the absence of irritation and allergenic effects. Owing to their favorable permeability properties with respect to various salts, nutrients, water and diverse other components of tear fluid and gases (CO₂ and O₂), the novel contact lenses have no effect, or virtually no effect, on the natural metabolic processes in the cornea. In contrast to many other siloxane-containing contact lenses, the present innovative extended-wear lenses have chemical and mechanical properties and ion permeability sufficient to avoid the undesired binding effect. Furthermore, the novel contact lenses have high dimensional stability and shelf life.

It must be emphasized that this balance of properties, especially the high ion permeability in combination with the high oxygen permeability, is key to producing a true extended-wear contact lens. The high oxygen permeability is required to prevent corneal swelling, thereby reducing the likelihood of ocular damage and wearer discomfort during periods of extended wear. The high ion permeability enables the lens to move on the eye such that corneal health is not substantially altered and wearer comfort is acceptable during a period of extended, continuous contact with ocular tissue and ocular fluids.

The preferred extended-wear contact lenses of the present invention are those which are comfortable over the period of extended wear. If the lens diameter is too small, the eyelids will not cover any portion of the lens when the eye is open. Thus, the eyelids will contact the edge of the lens each time the eyelid is closed. This repeated eyelid-lens interaction typically causes irritation, wearer discomfort, and lens dislodgement. Accordingly, the preferred contact lens diameters are those which are sufficiently large to minimize eyelid-lens interaction and the associated irritation. Preferably, the contact lens has a diameter of about 12 to about 16 millimeters, more preferably about 13 to 15 mm, and most preferably about 13.5 to 14.8 mm.

V. Methods of use as Extended-wear Lenses

The above-described ophthalmic lenses have special utility as extended-wear contact lenses. Contact lenses having sufficient oxygen and water transmission rates from inner (base curve) to outer (front curve) surface may be continuously worn for long periods of time without substantial corneal swelling or wearer discomfort. The method of wear includes (a) applying the lens to the eye and (b) allowing the lens to remain in intimate contact with the eye and tear fluids for a period of at least 24 hours without substantial adverse impact on corneal health or wearer comfort.

A preferred method includes additional steps of (c) removing the lens from the ocular environment; (d) treating the lens (i.e., disinfecting or cleaning the lens); (e) re-applying the lens to the eye; and (f) allowing the lens to remain in intimate contact with the eye and tear fluids for a period of at least an additional 24 hours without substantial adverse impact on corneal health or wearer comfort.

In a preferred embodiment, the lens is worn for a continuous period of at least four (4) days without substantial corneal swelling or wearer discomfort. In another preferred embodiment, the lens is worn for a continuous period of at least seven (7) days without substantial corneal swelling or wearer discomfort. In another preferred embodiment, the lens is worn for a continuous period of at least 14 days

45

without substantial corneal swelling or wearer discomfort. In yet another preferred embodiment, the lens is worn for a continuous period of at least 30 days without substantial corneal swelling or wearer discomfort.

VI. Methods of Manufacture

The ophthalmic lens may be manufactured, generally, by thoroughly mixing the oxyperm and ionoperm polymerizable materials, applying an appropriate amount of the mixture to a lens mold cavity, and initiating polymerization. Photoinitiators, such as those commercially available photoinitiators disclosed above, may be added to the prepolymerization mixture to aid in initiating polymerization. Polymerization may be initiated by a number of well known techniques, which, depending on the polymerizable material, may include application of radiation such as microwave, thermal, e-beam and ultraviolet. A preferred method of initiating polymerization is by application of ultraviolet radiation.

It has been discovered that the ion and/or water permeability of some of the aforementioned core materials may be increased by initiating and completing polymerization in an atmosphere which is substantially free of oxygen. Suitable gases which are readily commercially available include, without limitation thereto, nitrogen and carbon dioxide. Thus, in a preferred embodiment, the oxyperm and ionoperm polymerizable materials are polymerized in an atmosphere having less than about 10000 ppm oxygen. More preferably, the atmosphere surrounding the polymerizable material contains less than about 1000 ppm oxygen. Even more preferably, the surrounding atmosphere contains less than about 100 ppm oxygen, while the most preferred oxygen content is less than about 20 ppm.

In the aforementioned embodiment, the prepolymer mixture must be degassed prior to polymerization. The degassing may be accomplished by a number of techniques known in the art. One technique for degassing the prepolymer mixture involves the use of a series of freezing and thawing steps which are repeated until the appropriate gas concentration level is achieved in the prepolymer mixture. This freeze/thaw method involves cooling the prepolymer mixture until the mixture solidifies, applying a vacuum to the solidified prepolymer mixture, discontinuing the vacuum, and thawing the prepolymer mixture until the mixture is again in liquid form. While this degassing technique is advantageous in a laboratory setting, other degassing techniques known in the art may be more advantageous for commercial lens manufacturing processes.

Alternatively, the atmosphere surrounding the lens mold may be include oxygen, under certain conditions. For example, if the lens mold halves seal adequately to one another and the lens mold material has a low rate of oxygen permeability (e.g., polypropylene), it is possible to polymerize a degassed prepolymer mixture in a mold surrounded by ambient air without reaching prepolymer oxygen concentrations sufficiently high to substantially reduce ion or water permeability of the final lens. Thus, in another preferred embodiment of double-sided molding, the lens is formed by the following steps: (1) the prepolymer mixture is degassed, (2) a lens mold half is filled with the prepolymer mixture, (3) the mold halves are sealed to one another, and (4) the polymerization is initiated to form the lens, where the lens mold halves are formed from a material having a low oxygen permeability and steps (2)-(4) may occur in the presence or absence of oxygen. In this embodiment, it is preferred that the lens molds are stored in an inert substantially oxygen-free atmosphere, e.g., nitrogen or carbon dioxide, prior to use.

46

An essential feature of the manufacturing methods of the present innovative lenses is that a balance of high oxygen permeability and high ion permeability is achieved. Manufacturing techniques and conditions which result in lowering either the oxygen permeability or the ion permeability below levels sufficient to maintain good corneal health and on-eye movement during periods of extended wear are unacceptable to produce the innovative extended-wear contact lenses of the present invention.

Preferably, the manufacturing method produces a contact lens having a Dk/t of at least 70 barrers/mm and a Ionoton Ion Permeability Coefficient of at least 0.2×10^{-6} cm²/sec. More preferably, the manufacturing method produces a contact lens having a Dk/t of at least 75 barrers/mm and a Ionoton Ion Permeability Coefficient of at least 0.3×10^{-6} cm²/sec. The manufacturing method preferably provides a contact lens having a Dk/t of at least 87 barrers/mm and a Ionoton Ion Permeability Coefficient of at least 0.4×10^{-6} cm²/sec.

The previous disclosure will enable one having ordinary skill in the art to practice the invention. In order to better enable the reader to understand specific embodiments and the advantages thereof, reference to the following examples is suggested. However, the following examples should not be read to limit the scope of the invention.

Examples A-D are arranged in accordance with the materials defined above. Thus, Examples A-1, A-2, etc. relate to Material "A" as defined above, Examples B-1, B-2, etc. relate to Material "B" as defined above, Examples C-1, C-2, etc. relate to Material "C", and Examples D-1, D-2, etc. relate to Material "D". Temperatures are stated in degrees Celsius unless otherwise specified.

Examples E, F and G are directed to demonstrating a correlation between on-eye movement and the Ionoton Ion Permeability Coefficient, the Ionoflux Ion Permeability Coefficient, and the Hydrodell Water Permeability Coefficient, respectively.

EXAMPLE A-1

A polysiloxane macromer is prepared by reacting, at room temperature (about 21 C), one mole equivalent (about 100 grams) of poly(dimethylsiloxane) dialkanol (Shin Etsu Chemical Co., Tokyo, Japan) having hydroxyethyl propoxy end groups with 2 mole equivalents (about 21.2 grams) of isophorone diisocyanate (Aldrich Chemical Co., Milwaukee, Wis.) in the presence of about 0.2 grams dibutyltin dilaurate catalyst (Pfaltz & Bauer, Inc., Waterbury, Conn.). After about 48 hours reaction time, 2.02 mole equivalents (about 38.7 grams) of poly(ethylene glycol) ("PEG", about 610 g/mol Mn, Dow Chemical Corp., Midland, Mich.) and about 0.17 grams of dibutyltin dilaurate (about 0.43% by weight PEG) are added to 80 grams of the reaction product from the prior step. Sufficient chloroform (Aldrich Chemical Co.) is added to the mixture to make the mixture homogeneous. This mixture is stirred at room temperature for about 15 hours. Next, the mixture is stirred for about 8 hours at a temperature of about 44 to 48 C, with the temperature held substantially constant by a surrounding oil bath. The chloroform is then evaporated, in order to achieve a final concentration of about 50% by weight solids, by stirring the mixture at room temperature for about 8 hours. Then, about 2.14 mole equivalents (about 10.4 grams) of isocyanatoethyl methacrylate ("IEM", Monomer Polymer, Inc., Feasterville, Pa.) is added to the mixture. Finally, the mixture is covered with aluminum foil and stirred at room temperature for about 17 hours, yielding a polysiloxane-containing macromer having a number-average molecular weight (Mn) of about 4000 grams per mole.

5,965,631

47

The macromeric solution is then polymerized, in the presence of about 0.5 weight percent DAROCUR® 1173 photoinitiator (Ciba-Geigy Corporation, Ardsley, N.Y.) to form contact lenses. Polypropylene contact lens molds are filled with the copolymer precursor solution. Ultraviolet light (about 300 to 400 nm) at about 3–6 mW/cm² is applied to the solution in the mold for about 3 hours at room temperature. The UV light, in conjunction with the photoinitiator, causes polymerization, thereby allowing the solution to form a contact lens having the shape of the mold. The lenses are extracted with isopropanol to remove the remaining chloroform solvent and any unreacted components. The product is a polysiloxane-containing polymeric contact lens.

Prior to taking oxygen permeability measurements, the lenses are hydrated by placing the lenses in isotonic buffered saline solution for at least eight hours. After hydration, if necessary because of handling, each lens is cleaned with MIRAFLOW® Daily Cleaner (CIBA Vision Corporation, Duluth, Ga.) to remove grease and lipids prior to testing. Excess MIRAFLOW® cleaner is removed by rinsing with saline or purified water.

Oxygen fluxes (J) are measured at 34 C in a wet cell (i.e., gas streams are maintained at about 100% relative humidity) using a Dk1000 instrument. Oxygen transmissibility, D_{k/t}, is determined as outlined in the portions of the specification relating to oxygen permeability and transmissibility.

EXAMPLE A-2

A polysiloxane macromer is first prepared substantially in accordance with the procedure described in Example A-1.

A copolymer precursor solution is prepared by mixing about 180 grams polysiloxane-containing macromer, about 15 grams 3-methacryloxypropyltris(trimethylsiloxy) silane (Shin Etsu), about 4 grams 2-hydroxyethyl methacrylate ("HEMA"), about one gram ethylene glycol dimethacrylate ("EDGMA"), and about one gram DAROCUR® 1173 photoinitiator at room temperature for about 16 hours.

The copolymer precursor solution is then polymerized to form contact lenses. Polypropylene contact lens molds are filled with the copolymer precursor solution. Ultraviolet light (about 300 to 400 nm) at about 3–6 mW/cm² is applied to the solution in the mold for about 3 hours at room temperature. The UV light causes polymerization, thereby allowing the solution to form a contact lens having the shape of the mold. The lens are extracted with isopropanol to remove remaining chloroform solvent and any unreacted components. A preferred resulting polymer contains about 81.8 weight percent polysiloxane macromer, about 13.6% TRIS, about 3.6% 2-hydroxyethyl methacrylate, and about 0.9% EDGMA. [059-87]

The contact lens is degassed by placing the lens under suitable vacuum for a period sufficient to remove substantially all gas from the lens matrix. Fully hydrated degassed contact lenses having this composition have a Dk of about 87 barrers, a water content of about 19 weight percent, and a modulus of elasticity of about 2.5 MPa.

EXAMPLE A-3

A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 19.5 weight percent polysiloxane macromer, about 47% TRIS, and about 33.5% N,N-dimethylacrylamide. Fully hydrated contact lenses having this composition have a Dk of about 49 barrers, a water

5,965,631

48

content of about 30 weight percent, and a modulus of elasticity of about 2.4 MPa.

EXAMPLE A-4

5 A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 30 weight percent polysiloxane macromer, about 50% TRIS, and about 20% N,N-dimethylacrylamide. Fully hydrated contact lenses having this composition have a Dk of about 76 barrers, a water content of about 20 weight percent, and a modulus of elasticity of about 1.3 MPa.

EXAMPLE A-5

15 A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 30 weight percent polysiloxane macromer, about 40% TRIS, and about 30% N,N-dimethylacrylamide. Fully hydrated contact lenses having this composition have a Dk of about 55 barrers, a water content of about 30 weight percent, and a modulus of elasticity of about 3.5 MPa.

EXAMPLE A-6

25 A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 30 weight percent polysiloxane macromer, about 60% TRIS, and about 10% N,N-dimethylacrylamide. Fully hydrated contact lenses having this composition have a Dk of about 110 barrers, a water content of about 8.7 weight percent, and a modulus of elasticity of about 2.6 MPa.

EXAMPLE A-7

30 A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 30 weight percent polysiloxane macromer and about 70% TRIS. Fully hydrated contact lenses having this composition have a Dk of about 128 barrers and a water content of about 4.9 weight percent.

EXAMPLE A-8

35 A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 30 weight percent polysiloxane macromer, about 45% TRIS, 5% fluoroacrylate, and about 20% N,N-dimethylacrylamide. Fully hydrated contact lenses having this composition have a Dk of about 69 barrers, a water content of about 20 weight percent, and a modulus of elasticity of about 1.4 MPa.

EXAMPLE A-9

40 A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 82 weight percent polysiloxane macromer, about 14.4% TRIS, and about 3.7% 2-hydroxyethyl methacrylate. Fully hydrated contact lenses having this composition have a Dk of about 96 barrers, a water content of about 19 weight percent, and a modulus of elasticity of about 1.8 MPa.

EXAMPLE A-10

45 A polysiloxane macromer is prepared substantially in accordance with the procedures described in Example A-1, but the polyethylene glycol has a molecular weight of about 660.

5,965,631

49

A contact lens is prepared substantially in accordance with the procedure described in Example 2, but having the final composition of about 81.9 weight percent polysiloxane macromer, about 13.6% TRIS, about 3.7% 2-hydroxyethyl methacrylate, and about 0.8% ethylene glycol dimethacrylate. Fully hydrated contact lenses having this composition have a Dk of about 81 barrers, a water content of about 20 weight percent, and a modulus of elasticity of about 1.4 MPa.

EXAMPLE A-11

A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 82 weight percent polysiloxane macromer, about 8.6% TRIS, about 4.9% fluoroacrylate, about 3.5% 2-hydroxyethyl methacrylate, and about 1% EDGMA. Fully hydrated contact lenses having this composition have a Dk of about 77 barrers, a water content of about 22 weight percent, and a modulus of elasticity of about 1.3 MPa.

EXAMPLE A-12

A contact lens is prepared substantially in accordance with the procedure described in Example A-1, but the polysiloxane macromer used has hydroxy-sec-butyl end groups as opposed to hydroxyethylpropoxy end groups. The fully hydrated contact lens, after degassing, has a Dk of about 70 barrers, about a 22 weight percent water content, and a modulus of elasticity of about 2.4 Mpa.

EXAMPLE B-1**Macromer Synthesis**

51.5g (50 mmol) of the perfluoropolyether Fomblin® ZDOL (from Ausimont S.p.A., Milan) having a mean molecular weight of 1030 g/mol and containing 1.96 meq/g of hydroxyl groups according to end-group titration is introduced into a three-neck flask together with 50mg of dibutyltin dilaurate. The flask contents are evacuated to about 20 mbar with stirring and subsequently decompressed with argon. This operation is repeated twice. 22.2 g (0.1 mol) of freshly distilled isophorone diisocyanate kept under argon are subsequently added in a counterstream of argon. The temperature in the flask is kept below 30° C. by cooling with a waterbath. After stirring overnight at room temperature, the reaction is complete. Isocyanate titration gives an NCO content of 1.40 meq/g (theory: 1.35 meq/g).

202 g of the α,ω -hydroxypropyl-terminated polydimethylsiloxane KF-6001 from Shin-Etsu having a mean molecular weight of 2000 g/mol (1.00 meq/g of hydroxyl groups according to titration) are introduced into a flask. The flask contents are evacuated to approx. 0.1 mbar and decompressed with argon. This operation is repeated twice. The degassed siloxane is dissolved in 202 ml of freshly distilled toluene kept under argon, and 100 mg of dibutyltin dilaurate (DBTDL) are added. After complete homogenization of the solution, all the perfluoropolyether reacted with isophorone diisocyanate (IPDI) is added under argon. After stirring overnight at room temperature, the reaction is complete. The solvent is stripped off under a high vacuum at room temperature. Microtitration shows 0.36 meq/g of hydroxyl groups (theory 0.37 meq/g). 13.78 g (88.9 mmol) of 2-isocyanatoethyl methacrylate (IEM) are added under argon to 247 g of the α,ω -hydroxypropyl-terminated polysiloxane-perfluoropolyether-polysiloxane three-block copolymer (a three-block copolymer on stoichiometric

50

average, but other block lengths are also present). The mixture is stirred at room temperature for three days. Microtitration then no longer shows any isocyanate groups (detection limit 0.01 meq/g). 0.34 meq/g of methacryl groups are found (theory 0.34 meq/g).

The macromer prepared in this way is completely colourless, and clear. It can be stored in air at room temperature for several months in the absence of light without any change in molecular weight.

10

EXAMPLE B-2**Macromer Synthesis**

The first step of the macromer synthesis described under Example B-1 is repeated. An isocyanate titration of the perfluoropolyether reacted with IPDI gives a content of 1.33 meq/g of NCO (theory 1.35 meq/g).

In a second step, 87.1 g of the α,ω -hydroxypropyl-terminated polydimethylsiloxane TegomerH-Si2111 (Th. Goldschmidt AG, Essen) having a mean molecular weight of 890 g/mol (2.25 meq/g of hydroxyl groups according to titration) are dissolved in 87 ml of toluene. After the reaction has been carried out as indicated under B-1 and the solvent has been removed, a hydroxyl group content of 0.66 meq/g is determined by microtitration (theory 0.60 meq/g). The resultant intermediate is in turn reacted with a stoichiometric amount of isocyanatoethyl methacrylate. Microtitration then no longer shows any isocyanate groups (detection limit 0.01 meq/g). 0.56 meq/g of methacryl groups are found (theory 0.53 meq/g). The macromer prepared in this way is completely colourless and clear and has a long shelf life.

EXAMPLE B-3**Macromer Synthesis**

The first step of the macromer synthesis described under Example B-1 is repeated, but using a different perfluoropolyether: Fomblin® ZDOLTX (from Ausimont S.p.A., Milan). This material is terminated by $O—CF_2—CH_2—(OCH_2CH_2)_n—OH$ (where n=0, 1 or 2). The material used has a mean molecular weight of 1146 g/mol, and contains 1.72 meq/g of hydroxyl groups according to end-group analysis. An isocyanate titration of the perfluoropolyether reacted with IPDI shows a content of 1.23 meq/g of NCO (theory 1.25 meq/g).

In the second step, a stoichiometric amount of Tegomer Hi-Si2111 and toluene are again added. After the reaction has been carried out as indicated under Example B-1 and the solvent has been removed, a hydroxyl group content of 0.63 meq/g is determined by microtitration (theory 0.58 meq/g). The resultant intermediate is in turn reacted with a stoichiometric amount of isocyanatoethyl methacrylate. Microtitration then no longer shows any isocyanate groups (detection limit 0.01 meq/g). 0.55 meq/g of methacryl groups are found (theory 0.51 meq/g). The macromer prepared in this way is completely colourless and clear and has a long shelf life.

EXAMPLE B-4**Macromer Synthesis**

The first step of the macromer synthesis described under Example B-1 is repeated, but 5.0 g of Fomblin/ZDOL and 2.18 g of IPDI are employed. When the reaction is complete, microtitration shows an isocyanate group content of 1.31 meq/g of hydroxyl groups (theory 1.36 meq/g).

The second step of the synthesis described under Example B-1 is likewise carried out analogously, the stoichiometric

5,965,631

51

ratio between isocyanate-terminated perfluoropolyether and hydroxypropyl-terminated polysiloxane being 2:3. After the reaction has been completed and the solvent has been removed, microtitration shows a content of 0.2 meq/g of hydroxyl groups (theory 0.18 meq/g).

The third step of the synthesis described under Example B-1 is likewise carried out analogously, IEM being employed in a precisely stoichiometric ratio. After the reaction, free isocyanate groups can no longer be detected (detection limit 0.01 meq/g). 0.19meq/g of methacryl groups are found (theory 0.19 meq/g).

EXAMPLE B-5**Production of Contact Lenses**

13.0 g of macromer from Example B-1 are dissolved in 5.6 g of ethanol (Fluka, puriss. p.a.) (70% by weight solution). After complete homogenization of the solution, 5.2 g of 3-tris(trimethylsiloxy)silylpropyl methacrylate (TRIS from Shin-Etsu, product No. KF-2801), 7.8 g of freshly distilled dimethylacrylamide (DMA) and 160 mg of photoinitiator Darocur® 1173 (Ciba) are added. This solution is filtered through a Teflon membrane having a pore width of 0.45 mm under an argon pressure of from 1 to 2 atm. The filtered solution is frozen in a flask in liquid nitrogen, the flask is evacuated under a high vacuum, and the solution is returned to room temperature with the flask sealed. This degassing operation is repeated twice. The flask containing the macromer/comonomer solution is then transferred into a glove box with an inert-gas atmosphere, where the solution is pipetted into dust-free contact-lens moulds made from polypropylene. The moulds are closed, and the polymerization reaction is effected by UV irradiation (15 mW/cm², 5 min.), with simultaneous crosslinking. The moulds are then opened and placed in ethanol, causing the resultant lenses to swell out of the moulds. The lenses are extracted for 24 hours with constantly replenished distilled dichloromethane and subsequently dried in a high vacuum. The dried lenses are equilibrated in phosphate-buffered physiological saline solution in autoclave-resistant vials and then autoclaved at 120° C. for 30minutes. All physical data measurements are carried out on autoclaved lenses.

The lenses produced in this way are characterized by the following values: oxygen permeability (Dk) 77 barrer (determined by the "wet" method described below), water content of the equilibrated lenses 32 percent by weight, elongation at break at 35° C. 360%, modulus of elasticity 30° C. 0.5 MPa (measured using a Minimat from Polymer Laboratories, UK).

"Wet" Measurement of the Oxygen Permeability

The oxygen permeability of a material is determined by the coulometric method. To this end, pre-autoclaved lenses are clamped in a holder and then covered on the upper side with a 2 cm layer of water. A gas mixture comprising 21% of oxygen and 79% of nitrogen is passed continuously through the water layer with swirling. The oxygen which diffuses through the lens is measured using a coulometric detector. The reference values are those measured on commercially available contact lenses using this method. Cibasoft/(CIBA-Vision, HEMA lens) gives a measurement of approx. 7–10 barrer, and Excelens/(CIBA-Vision, PVA lens) gives a measurement of approx. 22 barrer.

Unfortunately, the oxygen permeability of, for example, contact lenses is frequently given in the literature as a straight Dk value without further definition and frequently

52

without giving any reference material. These are usually values determined on dry material (dry measurement). A comparative measurement of the oxygen permeability of polymer B-5 shows the differences:

- 5 a) "wet" measurement: 77 barrer
- b) dry measurement: 158 barrer

EXAMPLE B-6

The process described under Example B-5 for the production of contact lenses is repeated, but the mixture of comonomers has the following composition (in percent by weight):

- 15 55% of macromer from Example B-1
- 22% of TRIS
- 22.5% of DMA
- 0.5% of Blemer® QA

EXAMPLE B-7

The process described under Example B-5 for the production of contact lenses is repeated, but the mixture of comonomers has the following composition (in percent by weight):

- 25 55% of macromer from Example B-1
- 22% of TRIS
- 23% of DMA

EXAMPLE B-8

Analogously to EXAMPLE B-5 (in weight percent):

- 35 40% of macromer from Example B-1
- 30% of TRIS
- 30% of DMA

EXAMPLE B-9

The process described under B-5 for the production of contact lenses is repeated, but a 70% by weight solution of the macromer in toluene is used instead of the 75% by weight solution in ethanol described above. The mixture of comonomers has the following composition (in per cent by weight):

- 45 55% of macromer from Example B-1
- 22% of TRIS
- 23% of DMA

EXAMPLE B-10

The process described under B-5 for the production of contact lenses is repeated, but a 70% by weight solution of the macromer in octamethylcyclotetrasiloxane is used instead of the 75% by weight solution in ethanol described above. The mixture of comonomers has the following composition (in per cent by weight):

- 55 55% of macromer from Example B-1
- 22% of TRIS
- 23% of DMA

Physical measurement data for the contact-lens materials from Examples B-5 to B-10 (O₂ Dk value, wet method) are presented in TABLE B-I:

5,965,631

53

TABLE B-I

Example	Water Content [%]	Dk [barrier]	Modulus of Elasticity [MPa]	Elongation at Break [%]
B-5	32	77	0.5	360
B-6	23.8	110	1.1	160
B-7	19.5	110	0.6	130
B-8	30.9	81	0.3	300
B-9	30			
B-10	25			

EXAMPLE B-11

About 10.0 grams of macromer from Example B-1 are dissolved in 3.3 grams of ethanol (Fluka, puriss. p.a.). After complete homogenization of the solution, about 4.0 grams of 3-tris(trimethylsiloxy)silylpropyl methacrylate (TRIS, from Shin-Etsu, product no. KF-2801), about 5.9 g. freshly distilled dimethylacrylamide (DMA), about 0.1 g. Blemer® QA (a methacrylate having quaternary ammonium substituents, Linz Chemie) and about 100 mg of photoinitiator Darocur® 1173 (Ciba) are added. The solution is filtered through a TEFILON membrane having a pore width of 0.45 mm under an argon pressure of from about 1 to 2 atm.

The filtered solution is frozen in a flask in liquid nitrogen, the flask is evacuated under a high vacuum, and the solution is returned to room temperature with the flask sealed. This degassing operation is repeated twice. The flask containing the macromer/comonomer solution is then transferred into a glove box with an inert gas atmosphere, where the solution is pipetted into dust-free, polypropylene contact lens molds. The molds are closed, and the polymerization reaction is effected by UV irradiation, with simultaneous crosslinking. The molds are then opened and placed in isopropyl alcohol, causing the resultant lenses to swell out of the molds. The lenses are extracted for about 24 hours with nearly continuous replenishing of isopropyl alcohol. Subsequently, the lenses are dried under high vacuum.

The dried contact lenses are equilibrated in autoclave-resistant vials in phosphate-buffered physiological saline solution, and then autoclaved for 30 minutes at about 120° C. Physical measurement data for the autoclaved lens is presented below:

Dk [barrer]: 93
water content [%]: 20.3%
modulus of elasticity [Mpa]: 0.96

EXAMPLE B-12

Lenses are prepared in accordance with the procedures described in Example B-11, but are subsequent surface treated as follows. The dried lenses are transferred into a plasma coating apparatus wherein they are surface treated in a methane/“air” mixture (“air”, as used here, denotes 79% nitrogen and 21% oxygen) for a period of about 5 minutes. The apparatus and plasma treatment process have been disclosed by H. Yasuda in “Plasma Polymerization”, Academic Press, Orlando, Fla. (1985), pages 319 forward.

The plasma-treated contact lenses are equilibrated in autoclave-resistant vials in phosphate-buffered physiological saline solution, and then autoclaved for 30 minutes at about 120° C. Physical measurement data for the plasma-coated autoclaved lens is presented below:

Dk [barrer]: 88

54
water content [%]: 21.8%
modulus of elasticity [Mpa]: 1.03

EXAMPLE B-13

5 Lenses are prepared in accordance with the procedures described in Example B-5, but the mixture of comonomers has the following composition, in weight percentages:

Macromer of Example B-1: 60%

TRIS: 25%

DMA: 15%

EXAMPLE B-14

15 Lenses are prepared in accordance with the procedures described in Example B-6, with the same comonomer composition, but the comonomers are dispensed into dust-free contact lens molds in ambient air atmosphere.

EXAMPLE C-1

Reaction of α,ω -bis-aminopropyl-dimethylpolysiloxane with D(+)-gluconic acid d-lactone:

20 Before the reaction, the amino-functionalized polydimethylsiloxane employed for the synthesis (X-22-161-C, Shin Etsu, JP) was finely dispersed in acetonitrile, extracted and then subjected to molecular distillation.

25 The following reactions take place with exclusion of H_2O . 200 g of purified amino-functionalized polydimethylsiloxane (0.375 meq of NH_2/g ; Mn(VPO) 3400–3900 (VPO, Vapour Pressure Osmometry)), dissolved in 200 ml of absolute THF, are slowly added dropwise to a suspension of 13.35 g (75 mmol) of D(+)-gluconic acid d-lactone in 50 ml 30 of absolute THF and the mixture is stirred at 40° C. for about 24 hours until the lactone has reacted completely. (Monitoring of the reaction by thin layer chromatography (TLC): silica gel; i-propanol/ H_2O /ethyl acetate 6:3:1; staining with Ce(IV) sulfate/phosphomolybdic acid solution (CPS reagent)). After the reaction, the reaction solution is 35 concentrated to dryness and the residue is dried under 3 Pa (0.03 mbar) for 48 hours. 213.3 g of α,ω -bis(3-gluconamidopropyl)-poly-dimethylsiloxane are obtained. Titration of the amino groups with perchloric acid shows a 40 conversion of the amino groups of more than 99.8%.

Reaction of α,ω -bis-3-gluconamidopropyl-dimethylpolysiloxane with IEM:

45 The product obtained above (213.3 g) is dissolved in 800 ml of absolute THF and the solution is heated to 40° C. with the addition of catalytic amounts of dibutyltin dilaurate (DBTDL). 14 g (90 mmol) of IEM in 20 ml of absolute THF are added dropwise to this solution over a period of about 4 hours. This corresponds to a concentration of 1.2 equivalents of IEM per gluconamide unit. The reaction is carried out in the course of 48 hours (monitoring of the reaction by IR spectroscopy detection of the NCO ties). The reaction solution is concentrated and the product is dried in a brown glass flask under 3 Pa (0.03 mbar) for 24 hours, while cooling with ice. 227.2 g of a colourless rubber-elastic product of high 55 optical transparency remain.

EXAMPLE C-2 to C-7

Further amino propyl-dimethylpolysiloxanes (PDMS) are reacted with a different amount of gluconolactone and concentrations of IEM analogously to Example C-1. The examples are summarized in Table C-I.

5,965,631

55

56

TABLE C-I

Poly (dimethyl siloxane) [PDMS]	g (mmol)	Amount of batch				
		PDMS				
Example	Name	Type	Mn	NH ₂ * of NH ₂)	Glu	IEM
C-1	X-22-161-C	term.	3400	2 200 (75)	13.4 (75)	14.0 (90.0)
C-2	X-22-161-C	term.	3400	2 200 (74)	13.4 (75)	25.7 (165.0)
C-3	X-22-161-C	term.	3400	2 200 (75)	13.4 (75)	29.2 (187.5)
C-4	PS 813	pen.	1200	1		
C-5	GP 4	pen.	3150	2.6		
C-6	GP 6	pen.	5960	3		
C-7	KF 8003	pen.	9700	4.7 200 (98)	17.5 (98)	18.2 (117.4)

Legend:

X-22-161-C and KF 8003 are products from Shin Etsu (Japan), PS813 is a product from Petrarch-H ls, GP4 and GP6 are products from Genesee.

*Amino groups per macromer chain

Glu: D(+) gluconic acid d-lactone

term: terminal

pen: pendent

EXAMPLE C-8

The reaction is carried out in accordance with Example C-1, but instead of D(+)gluconic acid d-lactone, 75 mmol of lactobionic acid 1,5-lactone, suspended in 50 ml of absolute THF, are added dropwise to a solution of amino-functionalized polydimethylsiloxane (X-22-161-C) in 180 ml of absolute THF and 20 ml of DMSO (pure, 99%). Titration of the amino groups with perchloric acid indicates a reaction conversion of 99% (<0.01 meq of NH₂/g). Here also, a colourless optically clear macromer is obtained.

EXAMPLE C-9 and C-10

The reactions are carried out analogously to Example C-1. However, the catalyst necessary for addition of the isocyanate onto the hydroxyl groups is varied. Instead of DBTDL, catalytic amounts of 1,4-diazabicyclo[2.2.2]octane (DABCO) or 4-dimethylamino-pyridine (DMAP) are added and the reaction is continued as described under Example C-1. In both cases, an optically clear, colourless rubber-elastic macromer results in a manner corresponding to Example C-1.

EXAMPLE C-11

The reaction is carried out analogously to Example C-1. In a manner corresponding to Example C-8, 0.1 mol of lactobionic acid 1,5-lactone is suspended in 50 ml of absolute THF and the suspension is added dropwise to a solution of amino-functionalized polydimethylsiloxane (KF-8003) in 180 ml of absolute THF and 20 ml of DMSO (pure, 99%). The reaction time is increased to about 48 hours. A residual content of 0.07 meq of NH₂/g can be detected, and is reacted completely by addition of the corresponding molar amount of D(+)gluconic acid d-lactone to the reaction solution. The colourless highly transparent product has a residual content of amino groups of <0.01 meq/g.

EXAMPLE C-12

52.09g (9.78 mmol) of purified amino-functionalized polydimethylsiloxane (X-22-161-C, Shin Etsu JP), dis-

solved in 110 ml of absolute THF, are initially introduced into the reaction vessel under an inert gas atmosphere, and 1.14 g (6.52 mmol) of D-glucaro-1,4:6,3-dilactone, dissolved in 20 ml of absolute THF, are added. The reaction solution is stirred at room temperature for 15 hours and then worked up in a manner corresponding to Example C-1. The amine content is 0.134 meq/g. The terminal amino groups of the resulting penta-block macromer are reacted with glutonolactone in the following reaction step. 41.84 g (5.146 meq of NH₂) of the above macromer and 0.917 g (5.15 mmol) of D(+)gluconic acid d-lactone are suspended in 300 ml of absolute THF and the suspension is stirred under nitrogen at 40° C. for 18 hours. The filtered solution is then concentrated and the residue is dried under 3 Pa (0.03 mbar) for 48 hours. A highly viscous optically clear substance having a residual content of amino groups of 0.013 meq/g results.

EXAMPLE C-13

Preparation of an Amino- and Perfluoroalkyl-functionalized Polydimethylsiloxane

3.0 ml of absolute toluene are added to 15 g of poly (dimethylsiloxane-co-methylhydrosiloxane) [Bayer Silo-
pren U-230; 10,000 g/mol; 2.3 mmol of Si—H/g], and 1.72 g (9.2 mmol) of allylphthalimide [CAS Reg. No. 5428-09-1] are then added. The mixture is frozen several times and the flask evacuated and then brought to room temperature again. The flask is then let down with argon. 0.7 ml of a 0.005 molar solution of Lamoreaux catalyst (prepared in accordance with U.S. Pat. No. 3,220,972, General Electric) in absolute toluene (100 ppm of Pt/mol of Si—H) is added and the mixture is heated to 80° C. After a reaction time of half an hour, a colourless, clear to slightly cloudy solution, the 1H-NMR spectrum of which no longer shows resonances of allylic hydrogen atoms, is obtained.

Thereafter, 6.2 g (15.3 mmol) of degassed allyl 1H,1H,2H,2H-perfluoroctyl ether are slowly added and the mixture is stirred at 80° C. for 2 hours. A 1H-NMR spectrum now shows a severely weakened resonance of the Si—H function at 4.6 ppm and an intense resonance at 0.5 ppm, which originates from Si—CH₂ hydrogen atoms.

5,965,631

57

3.0 ml of 1-hexene are then added in order to react the remaining excess of Si—H groups, which could otherwise cause crosslinking of the polymer when air later has access. The mixture is further stirred at 80° C. for another half an hour. The reaction mixture is then left to stand overnight. The product is purified over a silica gel column with hexane/ethyl acetate (3:2), the solvent is stripped off and the macromer is dried under a high vacuum. A colourless, clear, viscous product is obtained. The macromer purified in this way is taken up in 20 ml of hexane, 20 ml of methylamine [33% in ethanol] are added and the mixture is heated to 40° C. After 10–15 minutes, a white luminous precipitate separates out. After 30 minutes, the suspension is cooled and filtered and the precipitate is washed with a little hexane. The filtrate is evaporated and the residue is then dried under a high vacuum. Thereafter, the content of amino groups is determined by titrimetry (perchloric acid).

The resulting macromer is clear and viscous. The amino group content is 78.6% of theory. The total yield of macromer after the chromatographic purification is 75%.

Preparation of a Gluconamide

17.3 g (corresponding to an amine content of 5.4 meq) of this aminoalkyl-substituted product are dissolved in 20 ml of dried THF. The solution is repeatedly frozen, degassed and let down with argon. All the following operations are carried out in an argon atmosphere. 712 mg of D(+) -gluconic acid d-lactone (4 mmol) are then added. Because of the low solubility of the lactone, a suspension is initially obtained. After stirring overnight at 50° C., the solution is clear and the lactone has been used completely. The stoichiometric remaining amount of D(+) -gluconic acid d-lactone (260 mg, 1.46 mmol) is then added and the mixture is stirred again at 50° C. overnight. A trace of unreacted lactone is observed. Completion of the reaction is monitored by means of thin layer chromatography on silica gel plates with the mobile

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EXAMPLE C-14

phase 1-propanol/ethyl acetate/water (6:1:3). The silica gel plates are developed by means of Ce(IV) sulfate/phosphoromolybdic acid solution. Subsequent titration on amino groups yields a residual amino content of <0.1%. After filtration and removal of the solvent by distillation, a highly viscous clear macromer with 0.295 mequivalent of gluconamide per gram of macromer is obtained.

58

bottomed flask and the flask is flushed with N2 for half an hour, while cooling with ice. 1.44 g of macromer from Example C-1 are transferred to a round-bottomed flask with a nitrogen attachment, degassed under 3 Pa (0.03 mbar) for 24 hours and then dissolved in 2.7 g of ethanol which has been flushed with N2 for half an hour beforehand. The subsequent preparation of samples and the polymerization are carried out inside a glove box with exclusion of oxygen. The above monomer mixture and the macromer solution from Example C-1 are mixed, with the addition of 0.012 g (0.21 mmol) of Darocur® 1173 and the mixture is subjected to microfiltration (0.45 mm filter). 180 µl of this mixture are introduced into a polypropylene mould, which is then closed with an appropriate lid of polypropylene. The mixture is then irradiated with a UV-A mercury high pressure lamp in a nitrogen atmosphere in a UV oven equipped for this for 5 minutes. The lamps (5 each of the brand TLK40W/10R, Philips) are above and below the holder inserted. The irradiation intensity is 14.5 mW/cm2.

The polypropylene mould is opened and the finished discs or lenses are removed by soaking by means of a solvent mixture of methylene chloride and ethanol (2:3). The lenses and discs are extracted in ethanol at room temperature in special polypropylene cages for 48 hours and then dried at 40° C. under 10 Pa (0.1 mbar) for 24 hours (autoclaving at 120° C., 30 minutes). The discs show an E modulus of 1.1 MPa, a permeability to oxygen of 183 barrier and a hardness (Shore A) of 53.

EXAMPLE C-15 to C-19

Further polymers are prepared in a manner corresponding to Example C-14 (composition in percentages by weight). Table C-II shows examples C-15 to C-19 and the properties of the resulting materials measured on discs.

TABLE C-II

Example	Water Content [%]	Macromer from Example	Macromer weight percent	DMA weight percent	DMEA weight percent	TRIS weight percent	E modulus [Mpa]	Dk [barrer]
C-15	not measured	C-3	32.8	—	30	37.2	—	—
C-16	19.9	C-3	32.9	34.3	—	32.7	0.7	84
C-17	25.1	C-3	39.3	34.3	—	36.4	0.9	72
C-18	17.5	C-3	35.7	34.3	—	30.0	0.7	100
C-19	23.4	C-3	33.3	33.3	—	33.4	0.7	96

Legend:

DMA: N,N-Dimethylacrylamide

TRIS: 3-Methacryloyloxypropyl-tris(trimethylsilyloxy)silane

DMEA: 2-Dimethylaminoethyl acrylate

EXAMPLE C-20

Uncoated Contact Lens

A contact lens is prepared in a manner corresponding to Example C-14, using the Example C-3 macromer, with the following composition in percentages by weight:

Macromer: 33.3

DMA: 33.3

TRIS: 33.4

The lens has a Dk of about 94 and a water content of about 20.0 weight percent. The results are presented in TABLE C-III for comparison with coated lens properties.

EXAMPLE C-14

Before the polymerization, the acrylates employed, isobutyl acrylate (IBA), N,N-dimethylacrylamide (DMA) and 3-methacryloyloxypropyl-tris(trimethylsilyloxy)silane (TRIS) are each freed from inhibitors by distillation. 0.32 g (2.76 mmol) of IBA, 0.80 g (8.1 mmol) of DMA and 1.44 g (3.4 mmol) of TRIS are weighed into a 50 ml round-

5,965,631

59

EXAMPLE C-21

Plasma-treated Contact Lens

Dried lenses prepared in accordance with the procedures described in Example C-20 are transferred into a plasma coating apparatus where the lenses are surface treated in a methane/“air” mixture (“air”, as used here, denotes 79% nitrogen and 21% oxygen). The apparatus and plasma treatment process have been disclosed by H. Yasuda in “Plasma Polymerization”, Academic Press, Orlando, Fla. (1985), pages 319 forward.

The dried plasma-treated contact lenses are equilibrated in autoclave-resistant vials in phosphate-buffered physiological saline solution, and then autoclaved for 30 minutes at about 120° C. The plasma-treated autoclaved lens has a Dk [barrier] of 90 and a water content of 21.5%. The results are presented in TABLE C-III for comparison with coated lens properties.

TABLE C-III

Example	Surface type	Dk [barrier]	Water content [%]
C-20	untreated	94	20.0
C-21	plasma-treated	90	21.5

EXAMPLE C-22

The synthesis of this polymer corresponds to Example C-14 with the following comonomer composition: Example C-3 macromer/TRIS/DMA: 32.8%/32.6%/34.2% (in percentages by weight) and an addition of 0.4% by weight of trimethylammonium-2-hydroxypropyl methacrylate hydrochloride (Blemer® QA, Nippon Oil Corp.). The polymer has a modulus of 0.9 MPa and a permeability to oxygen of 2 barrier. The water content is 25.1% (after 30 minutes’ autoclaving at 120° C.). For comparison, Example C-16 has a water content of 20% with a very similar comonomer composition (no addition of Blemer® QA).

EXAMPLE C-23

The polymer is prepared analogously to Example C-14, but the polymerization is carried out in bulk, which means without addition of ethanol. The composition of the comonomers and the material properties of the polymer synthesized, measured on discs is given below.

Example C-7 macromer: 41%

IBA: 23%

1-vinyl-2-pyrrolidone (NVP): 24%

acrylonitrile (AN): 12%

Hardness (shore A): 68

EXAMPLE C-24

The polymerization is carried out in accordance with Example C-14 but with the following changed comonomer composition:

macromer of Example C-7/IBA/TRIS 20%/19%/60% and 1% (in percentages by weight) of bis(3-methacryloyloxypropyl)tetra methylsiloxane.

An optically clear polymer with an E modulus of 0.4 MPa, a permeability to oxygen of 241 barrier and a hardness (Shore A) of 42 is obtained.

60

EXAMPLES C-25 through C-27

Contact lenses are prepared in accordance with the procedure described in Example C-14. The compositions in weight percentages are as follows:

Ex-	Macro-	Macromer	IBA weight	DMA	TRIS	HFBA
ample	mer	weight percent	percent	weight percent	weight percent	weight percent
C-25	C-3	36.0	8.0	20.0	36.0	—
C-26	C-2	35.0	5.0	20.0	35.0	5.0
C-27	C-3	32.8	—	30.0	37.2	—

where IBA is isobutylacrylate,

DMA is N,N-Dimethylacrylamide

TRIS is 3-methacryloyloxypropyl-tris(trimethylsiloxy) silane

HFBA is acrylsaure-2,2-3,4,4-hexafluorbutylester

EXAMPLE C-28

20 The polymerization is carried out in accordance with Example C-14 but with the following changed comonomer composition: macromer of Example C-1/DMA/TRIS 33.3%/33.3%/33.3%. An optically clear polymer is obtained.

EXAMPLE D-1

Macromer Synthesis

In a dry box under nitrogen atmosphere, about 200 grams 30 of dry PDMS dipropoxymethanol (Shin-Etsu) is added to a container. Isocyanatoethyl methacrylate (IEM) in an amount equal to about 2 moles per mole PDMS dialkanol is added to the container. About 0.1 weight percent dibutyltin dilaurate (DBTL) catalyst, based on PDMS dialkanol weight, is 35 added to the container along with a stir bar. The container is immersed in an oil bath atop a stir plate, and secured in place with a clamp. A stream of UPC air at about 2 psig is passed over the mixture. The mixture is agitated at room temperature (about 22° C.) for about 24 hours. An iterative procedure follows in which the mixture is analyzed for isocyanate content and IEM is added if the PDMS dialkoxyalkanol has 40 not been completely reacted. The mixture is stirred about 24 hours more. The macromer produced is a siloxane-containing macromer.

EXAMPLE D-2

Lens Fabrication

A prepolymerization mixture is prepared by mixing about 55 56 grams of the macromer from Example D-1, about 14 grams of TRIS, about 29 grams N,N-dimethylacrylamide (DMA), about 1 gram methacrylic acid, about 0.5 grams Darocur® 1173 photoinitiator, and about 20 grams hexanol. The mixture is agitated for about 20 minutes at room 60 temperature.

Next, the mixture is degassed via a series of freezing and thawing steps. The container is placed in a liquid nitrogen bath until the mixture solidifies. A vacuum is applied to the container at a pressure of about 200 millitorr or less for about 5 minutes. Then, the container is placed in a bath of room temperature water until the mixture is liquid again. This process is performed a total of three times.

The mixture is then polymerized to form contact lenses. The prepolymerization mixture is poured into polypropylene contact lens molds in a nitrogen atmosphere. The polymerization is effected by applying UV radiation (about 4–6 mW/cm²) for a period of about 15 minutes.

5,965,631

61

The resulting fully hydrated contact lens has a water content of about 23%. The lens has a Dk of about 115 barrers and a modulus of elasticity of about 2 MPa.

EXAMPLE D-3**Lens Fabrication**

A contact lens is prepared in accordance with the procedure described in Example D-2, with the difference being that the composition is about 50% macromer of Example D-1, about 20% TRIS and about 30% DMA.

The resulting fully hydrated contact lens has a water content of about 20%. The lens has a Dk of about 118 barrers and a modulus of elasticity of about 1.8 Mpa.

EXAMPLE E-1**Material A**

A contact lens is prepared substantially in accordance with the procedure described in Example A-2. Prior to polymerization, the prepolymerization mixture is degassed by cooling the prepolymer mixture with liquid nitrogen until the mixture solidifies and is near liquid nitrogen temperature, then applying a vacuum (about 0.1 mm Hg) to the solidified prepolymer mixture, discontinuing the vacuum, and thawing the prepolymer mixture until the mixture is again in liquid form. This degassing procedure is performed a total of three times on the prepolymerization mixture.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 19%. Subsequent to curing, the lens is plasma treated for about 10 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume:volume ratio. The working pressure of the gas is about 50 millitorr. The plasma treatment is accomplished in a Plasma Polymerization Apparatus LCVD-20-400A (Plasmacarb, Bedford, Mass.).

The Ionoton Ion Permeability Coefficient of the lens is 0.81×10⁻³ cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-2**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-10. Prior to polymerization, nitrogen gas is bubbled through the prepolymer mixture in order to remove oxygen from the prepolymer mixture.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 26 weight percent. No coating is applied to the surface.

The Ionoton Ion Permeability Coefficient of the lens is -0.063×10⁻³ cm²/sec. Clinical examination shows that the lens does not move on the human eye. See Table E for a summary of the results.

EXAMPLE E-3**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-12. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

62

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 30 weight percent. Subsequent to curing, the lens is plasma treated for about 3 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is 0.50×10⁻³ cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-4**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-12. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 30 weight percent. Subsequent to curing, the lens is plasma treated for about 5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is 0.47×10⁻³ cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-5**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-12. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 30 weight percent. Subsequent to curing, the lens is plasma treated for about 7.5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is 0.35×10⁻³ cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-6**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-11. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 30 weight percent. The lens is not subsequently coated.

The Ionoton Ion Permeability Coefficient of the lens is 1.1×10⁻³ cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-7**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-21. Prior to

5,965,631

63

polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is plasma treated for about 5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.⁵

The Ionoton Ion Permeability Coefficient of the lens is 2.9×10⁻³ cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-8**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-21. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is plasma treated for about 7.5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is 0.25×10⁻³ cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.²⁰

EXAMPLE E-9**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-20. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in an air atmosphere to form the contact lens. Subsequent to curing, the lens is not surface treated.

The Ionoton Ion Permeability Coefficient of the lens is 0.008×10⁻³ cm²/sec. Clinical examination shows that the lens does not move on the human eye. See Table E for a summary of the results.⁴⁰

EXAMPLE E-10**Material D**

A contact lens is prepared substantially in accordance with the procedure described in Example D-2. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is not surface treated.

5,965,631

64

The Ionoton Ion Permeability Coefficient of the lens is 1.4×10⁻³ cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-11**Material D**

¹⁰ A contact lens is prepared substantially in accordance with the procedure described in Example D-2. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

¹⁵ The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is plasma treated for about 7.5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

²⁰ The Ionoton Ion Permeability Coefficient of the lens is 0.61×10⁻³ cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-12**Material D**

²⁵ A contact lens is prepared substantially in accordance with the procedure described in Example D-2. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

³⁰ The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is plasma treated for about 5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

³⁵ The Ionoton Ion Permeability Coefficient of the lens is 1.5×10⁻³ cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E-I for a summary of the results.

EXAMPLE E-13**Material D**

⁴⁰ A contact lens is prepared substantially in accordance with the procedure described in Example D-2. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

⁴⁵ The prepolymer mixture is cured in an air atmosphere to form the contact lens. Subsequent to curing, the lens is not surface treated.

⁵⁰ The Ionoton Ion Permeability Coefficient of the lens is -0.001×10⁻³ cm²/sec. Clinical examination shows that the lens does not move on the human eye. See Table E for a summary of the results.

TABLE E

Example	Material	Degassing	Curing atmosphere	Surface treatment CH ₄ : air plasma [minutes]	Ionoton Ion Permeability Coefficient [10 ⁻³ cm ² /sec]	On-eye Movement
E-1	A	3-cycle freeze/thaw	nitrogen	10	0.81	YES
E-2	B	nitrogen bubble	nitrogen	no plasma	-0.063	NO

TABLE E-continued

Example	Material	Degassing	Curing atmosphere	Surface treatment CH ₄ : air plasma [minutes]	Ionon Ion Permeability Coefficient [10 ⁻³ cm ² /sec]	On-eye Movement
E-3	B	3-cycle freeze/thaw	nitrogen	3	0.50	YES
E-4	B	3-cycle freeze/thaw	nitrogen	5	0.47	YES
E-5	B	3-cycle freeze/thaw	nitrogen	7.5	0.35	YES
E-6	B	3-cycle freeze/thaw	nitrogen	no plasma	1.1	YES
E-7	C	3-cycle freeze/thaw	nitrogen	5	2.9	YES
E-8	C	3-cycle freeze/thaw	nitrogen	7.5	0.25	YES
E-9	C	3-cycle freeze/thaw	air	no plasma	0.008	NO
E-10	D	3-cycle freeze/thaw	nitrogen	no plasma	1.4	YES
E-11	D	3-cycle freeze/thaw	nitrogen	7.5	0.61	YES
E-12	D	3-cycle freeze/thaw	nitrogen	5	1.5	YES
E-13	D	3-cycle freeze/thaw	air	no plasma	-0.001	NO

Considering Examples E-1 through E-13 of Table E, the lowest value of Ionon Ion Permeability Coefficient for which a lens moves on the eye is 0.25×10^{-3} cm²/sec. The highest value of Ionon Ion Permeability Coefficient for a lens which bound on the eye is 0.008×10^{-3} cm²/sec. Thus, a contact lens preferably has an Ionon Ion Permeability Coefficient greater than about 0.008×10^{-3} cm²/sec., more preferably greater than about 0.25×10^{-3} cm²/sec.

EXAMPLE F-1

Material C

A contact lens is prepared substantially in accordance with the procedure described in Example C-25. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 0 mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone (PVP) in accordance with the following procedure, using a glass plasma reactor equipped with an external ring electrode and a 27.13 MHz radio frequency (RF) generator for the generation of an inductively-coupled, cold glow discharge plasma. Highly purified argon is used as a plasma gas and as a carrier gas for N-vinylpyrrolidone (NVP) monomer feed. The NVP feed line is located about 10 cm below the glow zone.

The contact lens is placed in the 20 cm diameter plasma reactor at a position about 15 cm below the plasma glow zone. The reactor is then evacuated for about 30 minutes to about 0.009 mbar. Subsequent to evacuation, the plasma gas flow is set to 20 sccm (standard cubic centimeters), the glow discharge is started at a pressure of about 0.15 mbar and maintained for about one minute at a power of about 170 Watts (in order to clean and activate the lens surface). After reduction of argon plasma gas flow to about 10 sccm, the argon carrier gas flow for the NVP monomer is also set to 10 sccm. The temperature of the NVP source (with the carrier gas bubbling through the liquid NVP) is held at about 40° C. The lenses are treated for about 10 minutes with a pulsing glow discharge plasma (1 μ sec. on, 3 μ sec. off) at about 0.35 mbar pressure and about 150 Watts power.

After interrupting the glow discharge and the carrier gas flow, the reactor is continuously purged with a 20 sccm argon stream at a pressure of about 0.009 mbar for about 30 minutes, in order to remove residual monomer and activated species. The PVP coated contact lenses thus produced are highly wettable and show the following contact dynamic contact angles, measured with a KRUESS (Hamburg, Germany) K-12 instrument:

	Untreated	Treated
Advancing	102	38
Receding	48	23
Hysteresis	53	15

Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-2

Material C

A contact lens is prepared substantially in accordance with the procedure described in Example C-26. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 2.8×10^{-7} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-3

Material C

A contact lens is prepared substantially in accordance with the procedure described in Example C-27. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 9.3×10^{-7} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example

5,965,631

67

F-1. Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-4**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-18. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 2.6×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-5**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-16. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 1.3×10^{-5} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-6**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-19. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 2.7×10^{-5} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-7**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-17. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 7.8×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-8**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-13. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 1.5×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-9**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-14. Prior to

5,965,631

68

surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 1.1×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-10**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-7. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 3.8×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-11**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-6. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 8.5×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-12**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-5. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 7.1×10^{-5} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

TABLE F

EX- AMPLE	MATERIAL (Example reference number)	IONOFLUX ION PERMEABILITY COEFFICIENT* [mm ² /min]	ON-EYE MOVEMENT CLINICAL DETERMINATION
F-1	C-25	0	NO
F-2	C-26	0.28×10^{-6}	NO
F-3	C-27	0.93×10^{-6}	NO
F-4	C-18	2.6×10^{-6}	YES
F-5	C-16	13.0×10^{-6}	YES
F-6	C-19	27.0×10^{-6}	YES
F-7	C-17	7.8×10^{-6}	YES
F-8	B-13	1.5×10^{-6}	NO
F-9	B-14	1.1×10^{-6}	NO
F-10	B-7	3.8×10^{-6}	YES
F-11	B-6	8.5×10^{-6}	YES
F-12	B-5	71.0×10^{-6}	YES

*All Ionoflux Ion Permeability Coefficients were determined on uncoated lenses.

Considering only Examples F-1 through F-13 of Table F, the lowest value of Ionoflux Ion Permeability Coefficient for which a lens moves on the eye is 2.6×10^{-6} mm²/min. The highest value of Ionoflux Ion Permeability Coefficient for a

69

lens which binds on the eye is 1.5×10^{-6} mm²/min. Thus, a contact lens preferably has an Ionoflux Ion Permeability Coefficient greater than about 1.5×10^{-6} mm²/min., more preferably greater than about 2.6×10^{-6} mm²/min.

EXAMPLE G-1

A contact lens is prepared substantially in accordance with the procedure described in Example A-2. The Hydrodell Water Permeability Coefficient is determined to be about 0.71×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-2

A contact lens is prepared substantially in accordance with the procedure described in Example B-5. The Hydrodell Water Permeability Coefficient is determined to be about 1.09×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-3

A contact lens is prepared substantially in accordance with the procedure described in Example B-6. The lens is surface treated in a plasma gas in accordance with the procedure described in Example F-1. The Hydrodell Water Permeability Coefficient is determined to be about 0.27×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-4

A contact lens is prepared substantially in accordance with the procedure described in Example C-19. The lens is surface treated in a plasma gas in accordance with the procedure described in Example F-1. The Hydrodell Water Permeability Coefficient is determined to be about 0.37×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-5

A contact lens is prepared substantially in accordance with the procedure described in Example D-2. The Hydrodell Water Permeability Coefficient is determined to be about 1.26×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-6

A contact lens is prepared substantially in accordance with the procedure described in Example C-14. The Hydrodell Water Permeability Coefficient is determined to be about 0.08×10^{-6} cm²/second. Clinical tests show that the lens does not move on the eye. See Table G for a summary of the results.

TABLE G

MATERIAL (Example reference AMPLE number)	SURFACE TREAT- MENT	HYDRODELL WATER PERMEABILITY COEFFICIENT [cm ² /sec.]	ON-EYE MOVEMENT- CLINICAL DETERMINA- TION
G-1 A-2	none	0.71×10^{-6}	YES
G-2 B-5	none	1.09×10^{-6}	YES
G-3 B-6	PVP	0.27×10^{-6}	YES
G-4 C-19	PVP	0.37×10^{-6}	YES

TABLE G-continued

5	MATERIAL (Example reference EX- AMPLE number)	SURFACE TREAT- MENT	HYDRODELL WATER PERMEABILITY COEFFICIENT [cm ² /sec.]	ON-EYE MOVEMENT- CLINICAL DETERMINA- TION
	G-5 D-2	none	1.26×10^{-6}	YES
10	G-6 C-14	none	0.08×10^{-6}	NO

Considering only Examples G-1 through G-6 of Table G, the lowest value of Hydrodell Water Permeability Coefficient for which a lens moves on the eye is 0.27×10^{-6} cm²/sec. The highest value of Hydrodell Water Permeability Coefficient for a lens which binds on the eye is 0.08×10^{-6} cm²/sec. Thus, a contact lens preferably has a Hydrodell Water Permeability Coefficient greater than about 0.08×10^{-6} cm²/sec., more preferably greater than 0.27×10^{-6} cm²/sec.

15 The invention has been described in detail, with reference to certain preferred embodiments, in order to enable the reader to practice the invention without undue experimentation. Theories of operation have been offered to better enable the reader to understand the invention, but such theories do not limit the scope of the invention. In addition, a person having ordinary skill in the art will readily recognize that many of the previous components, compositions, and parameters may be varied or modified to a reasonable extent without departing from the scope and spirit of the 20 invention. Furthermore, titles, headings, example materials or the like are provided to enhance the reader's comprehension of this document, and should not be read as limiting the scope of the present invention. Accordingly, the intellectual 25 property rights to the invention are defined by the following claims, reasonable extensions and equivalents thereof, as interpreted in view of the disclosure herein.

30 That which is claimed is:

1. An ophthalmic lens having ophthalmically compatible inner and outer surfaces, said lens being suited to extended 35 periods of wear in continuous, intimate contact with ocular tissue and ocular fluids, said lens comprising a polymeric material which has a high oxygen permeability and a high ion permeability, said polymeric material being formed from polymerizable materials comprising:

40 (a) at least one oxyperm polymerizable material and
(b) at least one ionoperm polymerizable material,

45 wherein said lens allows oxygen permeation in an amount sufficient to maintain corneal health and wearer comfort during a period of extended, continuous contact with ocular tissue and ocular fluids, and

50 wherein said lens allows ion or water permeation via ion or water pathways in an amount sufficient to enable the lens to move on the eye such that corneal health is not substantially harmed and wearer comfort is acceptable during a period of extended, continuous contact with ocular tissue and ocular fluids,

55 wherein said polymeric material has an oxygen permeability of at least about 84 barrers and said ophthalmic lens has an ion permeability characterized either by (1) an Ionoton Ion Permeability Coefficient of greater than about 0.2×10^{-6} cm²/sec or (2) an Ionoflux Diffusion Coefficient of greater than about 1.5×10^{-6} mm²/min, wherein said ion permeability is measured with respect to sodium ions.

60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 1225 1230 1235 1240 1245 1250 1255 1260 1265 1270 1275 1280 1285 1290 1295 1300 1305 1310 1315 1320 1325 1330 1335 1340 1345 1350 1355 1360 1365 1370 1375 1380 1385 1390 1395 1400 1405 1410 1415 1420 1425 1430 1435 1440 1445 1450 1455 1460 1465 1470 1475 1480 1485 1490 1495 1500 1505 1510 1515 1520 1525 1530 1535 1540 1545 1550 1555 1560 1565 1570 1575 1580 1585 1590 1595 1600 1605 1610 1615 1620 1625 1630 1635 1640 1645 1650 1655 1660 1665 1670 1675 1680 1685 1690 1695 1700 1705 1710 1715 1720 1725 1730 1735 1740 1745 1750 1755 1760 1765 1770 1775 1780 1785 1790 1795 1800 1805 1810 1815 1820 1825 1830 1835 1840 1845 1850 1855 1860 1865 1870 1875 1880 1885 1890 1895 1900 1905 1910 1915 1920 1925 1930 1935 1940 1945 1950 1955 1960 1965 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015 2020 2025 2030 2035 2040 2045 2050 2055 2060 2065 2070 2075 2080 2085 2090 2095 2100 2105 2110 2115 2120 2125 2130 2135 2140 2145 2150 2155 2160 2165 2170 2175 2180 2185 2190 2195 2200 2205 2210 2215 2220 2225 2230 2235 2240 2245 2250 2255 2260 2265 2270 2275 2280 2285 2290 2295 2300 2305 2310 2315 2320 2325 2330 2335 2340 2345 2350 2355 2360 2365 2370 2375 2380 2385 2390 2395 2400 2405 2410 2415 2420 2425 2430 2435 2440 2445 2450 2455 2460 2465 2470 2475 2480 2485 2490 2495 2500 2505 2510 2515 2520 2525 2530 2535 2540 2545 2550 2555 2560 2565 2570 2575 2580 2585 2590 2595 2600 2605 2610 2615 2620 2625 2630 2635 2640 2645 2650 2655 2660 2665 2670 2675 2680 2685 2690 2695 2700 2705 2710 2715 2720 2725 2730 2735 2740 2745 2750 2755 2760 2765 2770 2775 2780 2785 2790 2795 2800 2805 2810 2815 2820 2825 2830 2835 2840 2845 2850 2855 2860 2865 2870 2875 2880 2885 2890 2895 2900 2905 2910 2915 2920 2925 2930 2935 2940 2945 2950 2955 2960 2965 2970 2975 2980 2985 2990 2995 3000 3005 3010 3015 3020 3025 3030 3035 3040 3045 3050 3055 3060 3065 3070 3075 3080 3085 3090 3095 3100 3105 3110 3115 3120 3125 3130 3135 3140 3145 3150 3155 3160 3165 3170 3175 3180 3185 3190 3195 3200 3205 3210 3215 3220 3225 3230 3235 3240 3245 3250 3255 3260 3265 3270 3275 3280 3285 3290 3295 3300 3305 3310 3315 3320 3325 3330 3335 3340 3345 3350 3355 3360 3365 3370 3375 3380 3385 3390 3395 3400 3405 3410 3415 3420 3425 3430 3435 3440 3445 3450 3455 3460 3465 3470 3475 3480 3485 3490 3495 3500 3505 3510 3515 3520 3525 3530 3535 3540 3545 3550 3555 3560 3565 3570 3575 3580 3585 3590 3595 3600 3605 3610 3615 3620 3625 3630 3635 3640 3645 3650 3655 3660 3665 3670 3675 3680 3685 3690 3695 3700 3705 3710 3715 3720 3725 3730 3735 3740 3745 3750 3755 3760 3765 3770 3775 3780 3785 3790 3795 3800 3805 3810 3815 3820 3825 3830 3835 3840 3845 3850 3855 3860 3865 3870 3875 3880 3885 3890 3895 3900 3905 3910 3915 3920 3925 3930 3935 3940 3945 3950 3955 3960 3965 3970 3975 3980 3985 3990 3995 4000 4005 4010 4015 4020 4025 4030 4035 4040 4045 4050 4055 4060 4065 4070 4075 4080 4085 4090 4095 4100 4105 4110 4115 4120 4125 4130 4135 4140 4145 4150 4155 4160 4165 4170 4175 4180 4185 4190 4195 4200 4205 4210 4215 4220 4225 4230 4235 4240 4245 4250 4255 4260 4265 4270 4275 4280 4285 4290 4295 4300 4305 4310 4315 4320 4325 4330 4335 4340 4345 4350 4355 4360 4365 4370 4375 4380 4385 4390 4395 4400 4405 4410 4415 4420 4425 4430 4435 4440 4445 4450 4455 4460 4465 4470 4475 4480 4485 4490 4495 4500 4505 4510 4515 4520 4525 4530 4535 4540 4545 4550 4555 4560 4565 4570 4575 4580 4585 4590 4595 4600 4605 4610 4615 4620 4625 4630 4635 4640 4645 4650 4655 4660 4665 4670 4675 4680 4685 4690 4695 4700 4705 4710 4715 4720 4725 4730 4735 4740 4745 4750 4755 4760 4765 4770 4775 4780 4785 4790 4795 4800 4805 4810 4815 4820 4825 4830 4835 4840 4845 4850 4855 4860 4865 4870 4875 4880 4885 4890 4895 4900 4905 4910 4915 4920 4925 4930 4935 4940 4945 4950 4955 4960 4965 4970 4975 4980 4985 4990 4995 5000 5005 5010 5015 5020 5025 5030 5035 5040 5045 5050 5055 5060 5065 5070 5075 5080 5085 5090 5095 5100 5105 5110 5115 5120 5125 5130 5135 5140 5145 5150 5155 5160 5165 5170 5175 5180 5185 5190 5195 5200 5205 5210 5215 5220 5225 5230 5235 5240 5245 5250 5255 5260 5265 5270 5275 5280 5285 5290 5295 5300 5305 5310 5315 5320 5325 5330 5335 5340 5345 5350 5355 5360 5365 5370 5375 5380 5385 5390 5395 5400 5405 5410 5415 5420 5425 5430 5435 5440 5445 5450 5455 5460 5465 5470 5475 5480 5485 5490 5495 5500 5505 5510 5515 5520 5525 5530 5535 5540 5545 5550 5555 5560 5565 5570 5575 5580 5585 5590 5595 5600 5605 5610 5615 5620 5625 5630 5635 5640 5645 5650 5655 5660 5665 5670 5675 5680 5685 5690 5695 5700 5705 5710 5715 5720 5725 5730 5735 5740 5745 5750 5755 5760 5765 5770 5775 5780 5785 5790 5795 5800 5805 5810 5815 5820 5825 5830 5835 5840 5845 5850 5855 5860 5865 5870 5875 5880 5885 5890 5895 5900 5905 5910 5915 5920 5925 5930 5935 5940 5945 5950 5955 5960 5965 5970 5975 5980 5985 5990 5995 6000 6005 6010 6015 6020 6025 6030 6035 6040 6045 6050 6055 6060 6065 6070 6075 6080 6085 6090 6095 6100 6105 6110 6115 6120 6125 6130 6135 6140 6145 6150 6155 6160 6165 6170 6175 6180 6185 6190 6195 6200 6205 6210 6215 6220 6225 6230 6235 6240 6245 6250 6255 6260 6265 6270 6275 6280 6285 6290 6295 6300 6305 6310 6315 6320 6325 6330 6335 6340 6345 6350 6355 6360 6365 6370 6375 6380 6385 6390 6395 6400 6405 6410 6415 6420 6425 6430 6435 6440 6445 6450 6455 6460 6465 6470 6475 6480 6485 6490 6495 6500 6505 6510 6515 6520 6525 6530 6535 6540 6545 6550 6555 6560 6565 6570 6575 6580 6585 6590 6595 6600 6605 6610 6615 6620 6625 6630 6635 6640 6645 6650 6655 6660 6665 6670 6675 6680 6685 6690 6695 6700 6705 6710 6715 6720 6725 6730 6735 6740 6745 6750 6755 6760 6765 6770 6775 6780 6785 6790 6795 6800 6805 6810 6815 6820 6825 6830 6835 6840 6845 6850 6855 6860 6865 6870 6875 6880 6885 6890 6895 6900 6905 6910 6915 6920 6925 6930 6935 6940 6945 6950 6955 6960 6965 6970 6975 6980 6985 6990 6995 7000 7005 7010 7015 7020 7025 7030 7035 7040 7045 7050 7055 7060 7065 7070 7075 7080 7085 7090 7095 7100 7105 7110 7115 7120 7125 7130 7135 7140 7145 7150 7155 7160 7165 7170 7175 7180 7185 7190 7195 7200 7205 7210 7215 7220 7225 7230 7235 7240 7245 7250 7255 7260 7265 7270 7275 7280 7285 7290 7295 7300 7305 7310 7315 7320 7325 7330 7335 7340 7345 7350 7355 7360 7365 7370 7375 7380 7385 7390 7395 7400 7405 7410 7415 7420 7425 7430 7435 7440 7445 7450 7455 7460 7465 7470 7475 7480 7485 7490 7495 7500 7505 7510 7515 7520 7525 7530 7535 7540 7545 7550 7555 7560 7565 7570 7575 7580 7585 7590 7595 7600 7605 7610 7615 7620 7625 7630 7635 7640 7645 7650 7655 7660 7665 7670 7675 7680 7685 7690 7695 7700 7705 7710 7715 7720 7725 7730 7735 7740 7745 7750 7755 7760 7765 7770 7775 7780 7785 7790 7795 7800 7805 7810 7815 7820 7825 7830 7835 7840 7845 7850 7855 7860 7865 7870 7875 7880 7885 7890 7895 7900 7905 7910 7915 7920 7925 7930 7935 7940 7945 7950 7955 7960 7965 7970 7975 7980 7985 7990 7995 8000 8005 8010 8015 8020 8025 8030 8035 8040 8045 8050 8055 8060 8065 8070 8075 8080 8085 8090 8095 8100 8105 8110 8115 8120 8125 8130 8135 8140 8145 8150 8155 8160 8165 8170 8175 8180 8185 8190 8195 8200 8205 8210 8215 8220 8225 8230 8235 8240 8245 8250 8255 8260 8265 8270 8275 8280 8285 8290 8295 8300 8305 8310 8315 8320 8325 8330 8335 8340 8345 8350 8355 8360 8365 8370 8375 8380 8385 8390 8395 8400 8405 8410 84

5,965,631

71

for vision correction, contact lenses for eye color modification, ophthalmic drug delivery devices, and ophthalmic wound healing devices.

3. An ophthalmic lens of claim **1**, wherein said ophthalmic lens is a contact lens.

4. An ophthalmic lens of claim **1**, wherein said polymeric material has an oxygen permeability of at least about 90 barrers.

5. An ophthalmic lens of claim **4**, wherein said polymeric material has an oxygen permeability of at least about 105 barrers.

6. An ophthalmic lens of claim **5**, wherein said polymeric material has an oxygen permeability of at least about 112.5 barrers.

10

72

7. An ophthalmic lens of claim **5**, wherein said polymeric material has an oxygen permeability of at least about 130.5 barrers.

8. An ophthalmic lens of claim **6**, wherein said polymeric material has an oxygen permeability of at least about 140 barrers.

9. An ophthalmic lens of claim **7**, wherein said polymeric material has an oxygen permeability of at least about 150 barrers.

10. An ophthalmic lens of claim **8**, wherein said polymeric material has an oxygen permeability of at least about 174 barrers.

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